## Pharmaceuticals, Personal Care Products and Endocrine Disrupting Compounds in Groundwater

Pharmaceuticals, personal care products (PCPs) and endocrine disrupting compounds (EDCs) are a large group of substances present in human generated waste streams that potentially could contaminate groundwater resources. These substances are often classified, along with other chemicals, as contaminants of emerging concern (CECs), emerging contaminants (ECs) or trace organic contaminants (TOrCs).

Pharmaceuticals such as antibiotics, birth control pills and various prescription medicines may be present in wastewater effluents. PCPs, including shampoos, detergents and "over the counter" non-prescription medications, are found in both treated wastewater discharges and the municipal solid waste stream. EDCs adversely affect the behavior of natural hormones in humans and other animals. They include both anthropogenic chemicals, such as pesticides and plasticizers, and naturally occurring compounds like steroids and plant produced estrogens. EDCs are found in domestic and industrial wastewaters and in agricultural run-off. Some pharmaceutical and PCP compounds act as endocrine disruptors. New analytical methods, allowing detection of very small quantities of a substance, have helped improve investigations into the occurrence of emerging contaminants such as pharmaceuticals, PCPs and EDCs in the environment.

Discharges of treated wastewater through land (soil) treatment systems, leachate leaking from solid waste landfills, sludge biosolids landspreading activities and infiltration of polluted surface waters can potentially contaminate groundwater aquifers. The mobility and fate of discharged/released substances in the subsurface is a function of a variety of factors including the substance's adsorption and biodegradability properties and the amount and characteristics of any soil through which the substance percolates before reaching groundwater. Recent studies in other states have shown that pharmaceuticals, PCPs and EDCs can be present at sites where treated wastewater is used to recharge groundwater. In Wisconsin, research has been done evaluating the occurrence and movement in the subsurface of some pharmaceuticals, PCPs and EDCs.

A DNR and DATCP-funded study (Karthikeyan and Bleam, 2003), investigated the presence of antibiotics in treated wastewater effluents, and their potential fate in the subsurface. A variety of antibiotics were detected in wastewaters analyzed for the study. Two antibiotics, tetracycline and sulfamethoxazole, were found in all of the treated wastewater effluents tested for the project. Very small concentrations of these two antibiotics were also detected in groundwater monitoring wells located directly adjacent to one of the study land treatment system seepage discharge sites.

A UW-funded study (Pedersen and Karthikeyan, 2005) investigated the soil adsorption properties of common antibiotics. This study found that under certain soil conditions some antibiotics, such as the sulfonamide antibiotics, have the potential to be mobile in the subsurface. A number of additional studies, focused on specific antibiotic compounds, have evaluated the factors that affect antibiotic mobility and fate in the subsurface environment (Gao and Pedersen, 2005) (Gao and Pedersen, 2010) (Gu and Karthikian, 2005a) (Gu and Karthikian, 2005b) (Gu and others, 2007) (Gu and Karthikian, 2008) (Sibley, 2008) (Pedersen and others, 2009).

A study of the use of a screening assay to evaluate the occurrence of estrogenic endocrine disrupting chemicals in groundwater was conducted by the Wisconsin State Lab of Hygiene (Sonzogni and others, 2006). This study included testing of both high capacity water supply wells located in close proximity to surface waters into which treated wastewater effluent was being discharged, and water supply wells located in areas of home on-site wastewater-treatment-system discharge into groundwater. A breast

cancer cell line assay (E-screen assay) was used to test study samples for the presence of estrogenic endocrine disrupting compounds. Estrogenic EDCs were detected in surface waters tested but multiple groundwater samples from high-capacity water-supply wells located near those surface waters showed no estrogenic endocrine disruptor activity. Samples for estrogenic EDC analysis were collected from home on-site wastewater treatment systems and from groundwater monitoring wells located adjacent to two of the systems. Estrogenic activity was detected in wastewater treatment system effluent but was not detected in groundwater monitoring well samples.

A DNR project conducted in Dane County (Bradbury and Bahr, 2005) assessed groundwater impacts from on-site wastewater-treatment-system discharge. This project included an assessment of pharmaceuticals, PCPs and estrogenic EDCs in treatment system effluent, soil porewater and groundwater. Four compounds, acetaminophen (Tylenol), paraxanthine (caffeine metabolite) and the hormones estrone and  $\beta$ -estradiol, were detected in wastewater treatment system effluent samples. No pharmaceuticals, PCPs or estrogenic EDCs were detected in the groundwater or soil pore water samples collected for the study.

A UW study (Bauer-Dantoin, 2009) monitored the extent to which groundwater in northeastern Wisconsin is contaminated with endocrine disrupting chemicals (EDCs). The Silurian aquifer of northeastern Wisconsin may be particularly susceptible to nonpoint source contamination due to the existence of shallow soils, dolomite bedrock, and karst features, which combine to facilitate the transport of surface runoff to groundwater. Land application of manure containing synthetic and endogenous hormones may be a significant source of nonpoint source pollutants, including EDCs, to groundwater in the heavily farmed regions of northeast Wisconsin. This study used the MCF-7 breast cancer cell proliferation assay (E-screen) to determine if groundwater samples collected from four northeast Wisconsin counties, including Brown, Calumet, Fond du Lac, and Kewaunee, exhibited estrogenic behavior. Groundwater samples were collected four times between the summer of 2008 and the spring of 2009, and were analyzed for estrogenicity, 17β-estradiol concentrations, nitrate, conductivity, total coliform, enterococci, and E. coli. The wells chosen for this study were located in agricultural areas of northeast Wisconsin, were cased into the Silurian aquifer, and were chosen in light of past contamination with bacteria and/or nitrate. Estrogenic activity was detected in a portion of the groundwater samples during all four sampling periods, despite apparent toxicity and/or anti-estrogenic effects observed in the E-screen. The estradiol equivalents found in the study are below the range known to cause endocrine disruption in wildlife and are within the range of levels found in other studies that utilized the E-screen to analyze water samples. Unsafe levels of bacteria and nitrate occurred during all four sampling periods. Average bacterial contamination increased following snowmelt events in February and March 2009. Coliform, enterococci, and E. coli were positively correlated throughout the study, with the strongest correlations occurring in the March 2009 sampling period. Correlations were not found between nitrate and bacteria, or nitrate and estrogencity. One weak, positive correlation was found between E. coli and estrogenicity in the March 2009 sampling period.

A DNR project conducted by the Wisconsin State Laboratory of Hygiene explored the potential of hormones from livestock operations to contaminate groundwater. Water samples were collected during precipitation or snowmelt from agricultural fields and subsurface tiles and evaluated for hormones and hormone activity. Some samples did contain hormones (including estrogens, androgens and progesterone) in ng/L concentrations, and concentrations were usually lower in tile water samples than on the surface water samples. Additionally, groundwater samples were collected from monitoring wells at UW-Platteville Pioneer Farms. None of the groundwater samples had detectable levels of hormones or hormone activity, indicating that sorption by soil and degradation of hormones can occur and will protect groundwater at some sites.

The DNR is using the results of pharmaceutical, PCP and EDC research studies to evaluate whether current state groundwater protection regulations are adequate to address potential adverse impacts from the discharge of these substances. Studies comparing the levels of pharmaceuticals, PCPs and EDCs present in wastewater influent with treatment system effluent levels are providing information on the removal effectiveness of wastewater treatment processes. Research into the behavior of pharmaceutical, PCP and EDC substances in soil and groundwater is helping the DNR develop effective monitoring strategies. Studies evaluating new sampling techniques and analytical test methods have helped assure that the DNR is utilizing the best available tools to assess the occurrence of these substances in the environment.

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